Assessing Uncertainty in Mass Balance Calculation of River Nonpoint Source Loads

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Abstract: Several sources of uncertainty are considered in using field data to perform mass balance calculations to estimate nonpoint source (NPS) loads of total dissolved solids (TDS) and selenium (Se) to two reaches along the Lower Arkansas River in Colorado. This approach renders stochastic models of the mass balance equations for each river reach, where the input variables and their associated parameters are treated as random variables described by probability distributions. A data set collected in an intensive field effort conducted over several years is used in developing the models. Monte Carlo simulation solves the stochastic mass balance equations to describe distributions of possible values of the NPS loads. Results indicate that uncertainty in these calculated loads is sizeable. Annual average coefficient of variation (CV) in calculated total NPS TDS loads for sample periods within the two reaches ranges between 0.15 and 2.76, averaging about 1.1. For the Se mass balance along the downstream reach, the average CV in calculated loads is 0.23. The 90% prediction interval width for total NPS TDS load averaged over the 58 sample periods along the upstream reach is 13,691 (kg/day)/km, compared to an overall average mean load of 8,383 (kg/day)/km. It is 8,545 (kg/day)/km averaged over the 61 sample periods downstream, compared to an overall average mean load of 11,183 (kg/day)/km. For the Se load, the overall average 90% prediction interval width is also substantial compared to the overall average mean: 0.028 (kg/day)/km compared to 0.038 (kg/day)/km. Change in stored solute mass within the river over sample periods is found to be a major contributing factor to the calculation of NPS loads. Also, sensitivity analyses are performed that yield information on the relative influence that the degree of uncertainty in each random parameter has on the uncertainty in the calculated solute loads.

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Introduction

Preserving and enhancing the quality of river flows requires knowledge of the magnitude and the variability of suspended and dissolved chemical masses that move about within surface and subsurface waters. Chemical masses that travel to the river main stem and to its tributaries in flows that are distributed over relatively long stream reaches, in contrast to those that enter at well-defined and regulated points, are referred to as nonpoint source (NPS) loads. The assessment and control of NPS loads from both natural and human-induced sources remains perhaps the biggest challenge to managing the pollution of river environments (USEPA 2000). The urgency to meet this challenge can be seen in recent accelerated efforts by the US Environmental Protection Agency (USEPA) to administer the "total maximum daily load" (TMDL) program established in the 1972 Clean Water Act. This program requires states to identify and regulate TMDLs of pollutants to water bodies, including designated river reaches, which are required to meet water quality standards set for specific uses. Though pollution from most point sources has been successfully reduced through the regulations of the National Pollutant Discharge Elimination System (NPDES), the control of unregulated NPS pollution remains difficult (National Research Council 2001). Major efforts are now underway to identify and describe the nature and the severity of NPS pollution, and to identify best management practices (BMP) for activities that contribute to NPS loading of pollutants to water bodies (Ice 2004).

Of special concern in many arid and semiarid regions are river valleys that are affected by NPS loads induced by irrigation. Irrigation of agricultural lands often results in high concentrations of salt and other dissolved constituents in irrigation return flows to rivers. Irrigation return flows have higher solute concentrations than the original irrigation water diverted and applied to fields, due in part to evapotranspiration. In addition, the water in irrigation return flows can dissolve added chemicals as well as salts and metals that naturally occur in soils and geologic materials as the water moves over the land surface and through the underlying aquifer, further increasing constituent loads as it makes its way back to streams.

The ability to fully quantify NPS loads is always limited—in part due to financial, time, equipment, and manpower constraints, and in part due to the multilayered complexity of related natural processes. These limitations can be relaxed by investment in more and better data gathering, but only to an extent. Uncertainty at some level will always remain, and its presence engenders notions of risk, doubt, and caution in the decisions that must be made to manage NPS pollution. Hence, it is important not only to

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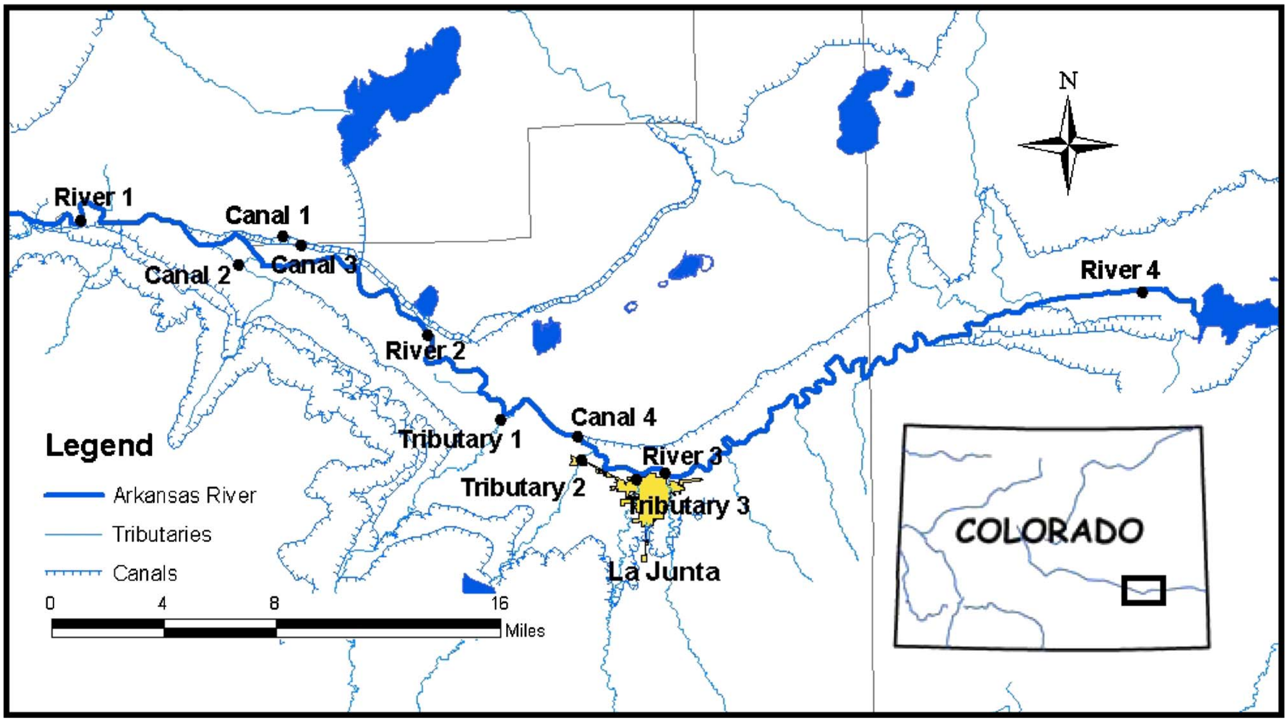

Fig. 1. Map of upstream reach along Arkansas River showing sampling locations that were utilized in stochastic mass balance model

understand the size and influence of various sources of data uncertainty but also to have an idea of their relative impact on the uncertainty in final estimates of NPS loads (National Research Council 2001).

NPS loads are commonly estimated by applying the conservation of mass principle to an identified reach along a river over a defined time period (Jaworski et al. 1992; Jain 1996; Jha et al. 2005). Measurements are made of water and solute concentrations associated with fluxes at the upstream and downstream ends of the reach, with fluxes that enter or leave at selected locations along the reach, and with changes in dissolved mass stored within the reach. Unmeasured NPS load accumulating to the river reach is then calculated as the unknown variable that brings closure to the mass balance equation. Estimates derived from this approach are characteristically obscure for a variety of reasons, including the following: errors in measuring fluxes, volumes, and concentrations at selected locations; considerable spatial and temporal variability in flows and concentrations that extend over large scales along river systems; and neglect or misspecification of processes that can affect the mass balance along the river.

This paper explores uncertainty in estimating NPS loads using a chemical mass balance applied to two reaches along the Lower Arkansas River Valley in Colorado. Estimates of salt, as total dissolved solids (TDS), and selenium (Se) loads were made. Data gathered from a total of 20 locations in the field were used in developing stochastic mass balance estimates of NPS loads as quantities whose uncertainty is derived from a number of different sources. This analysis provides insight into the magnitude of the ambiguity that is attached to typical mass balance estimates of NPS loads. Such information may prove helpful in judging the reliability of mass balance estimates as a foundation for formulating and implementing regulatory measures such as TMDLs and BMPs (Krupnick et al. 2006). Also, the relative contribution of each examined source of uncertainty to the degree of uncertainty in the final estimated NPS loads is studied using sensitivity analysis. Results suggest which data sources might merit additional attention in order to better describe or, in some cases, to reduce uncertainty in estimates of NPS loads.

Stochastic methods have been used by other researchers in modeling and evaluating aspects of river water quality (e.g., de Azevedo et al. 2000; Chiang and Gates 2004; Jha et al. 2005; Aulenbach and Hooper 2006). The distinctions of the current study are: (1) its attention to 13 specific sources of parametric uncertainty affecting the estimation of river NPS loads, drawing upon the results of an intensive field data collection effort; (2) its accounting for the effect of mass storage change in the stochastic calculations; and (3) its direct consideration of uncertainty sensitivity.

Study Site and Monitoring Program

A region greatly impacted by salinization from irrigated agriculture is the Lower Arkansas River Valley in southeastern Colorado (Burkhalter and Gates 2005). High salt concentrations in irrigation water diverted from the river have contributed to significant crop yield reduction. Se also has been identified as a NPS load of concern, since all segments of the Lower Arkansas River have been designated as impaired by concentrations that exceed aquatic habitat standards (Donnelly and Gates 2005). To estimate the magnitude of NPS loads throughout the river basin, mass balances of TDS were developed using measured flows and concentrations for two reaches along the river, referred to as the upstream reach and the downstream reach. A mass balance of dissolved Se was also developed for the downstream reach. The upstream study reach, near La Junta, Colo., extended approximately 91 km along the river (Fig. 1). The downstream study reach extended approximately 65 km along the river from Lamar, Colo., to just east of the Colorado–Kansas border (Fig. 2). Uncer-

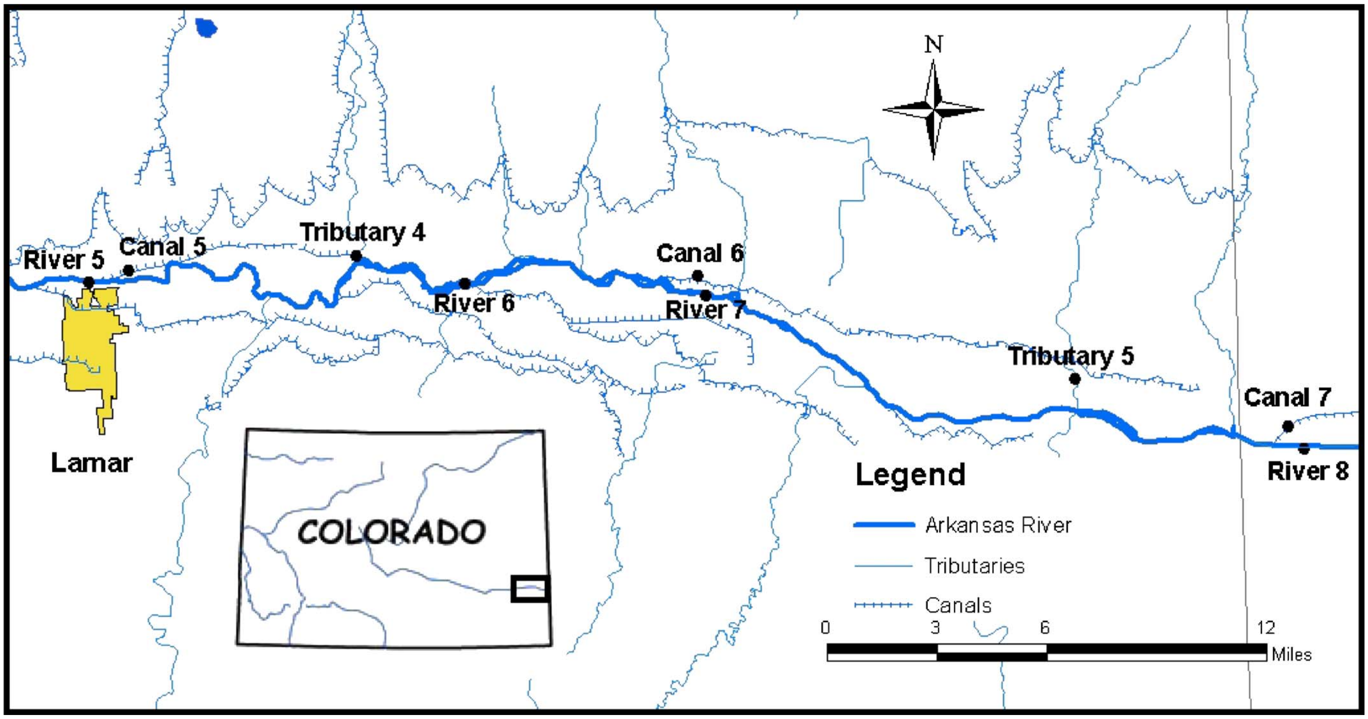

Fig. 2. Map of downstream reach along Arkansas River showing sampling locations that were utilized in stochastic mass balance model

tainty analyses of the load calculations were performed by identifying and describing several constituent load terms that could be estimated from field data, as random variables subject to several sources of uncertainty. These stochastic input variables were incorporated into the mass balance models in order to generate ranges of possible values for the NPS loads for TDS and Se.

In situ electrical conductivity (EC) measurements, standardized at 25° C, were made with a specific conductance probe, and water-quality samples for analysis of TDS and/or Se concentration (C_{Se}) were collected along the Arkansas River and near the mouths of selected tributaries. Water quality samples were gathered as grab samples and placed in clean 120 mL or 250 mL bottles using a peristaltic pump connected to decontaminated plastic tubing or, in the case of TDS samples upstream, by manually dipping the bottle or a plastic bucket sampler. Dissolved Se samples were filtered through a disposable capsule filter, preserved at a pH <2 by adding 5 mL of a 10% solution of ultrapure nitric acid in reagent water per liter of sample (approximately 0.625 mL per 120 mL sample bottle), and were stored on ice (at about 4°C).

EC measurements and water-quality samples were collected at 11 locations upstream and at nine locations downstream. For the TDS mass balance model for the upstream reach, there were 14 sample periods available in 2000, 13 in 2001, 14 in 2002, 11 in 2004, and six in 2005. Due to faulty specific conductance probes used in the upstream reach in 2003, data for 2003 were not available. For the downstream reach, there were 18 sample periods for TDS in 2002, 13 in 2003, 15 in 2004, and 15 in 2005. For the Se mass balance there were a total of 12 sample periods from 2003 to 2005. Each sample period in this study lasted for 1–3 days and sample periods along a given river reach were spaced at intervals ranging from less than 1 week to about 20 months between periods. Less than 15% of the total of 131 sample periods for which data were analyzed exceeded 2 days in duration. Additional samples, gathered previously from the study reaches, were used in developing relationships between EC and TDS and between EC and C_{Se}. Samples were analyzed in a laboratory for TDS by summing the concentrations of major cations (sodium, potassium, calcium, magnesium) and anions (nitrate, sulfate, chloride, carbonate, bicarbonate, and boron) using standard analytical procedures recommended by the Environmental Protection Agency (EPA) and/or described in Greenberg et al. (1992) and Herlich (1990). Water-quality samples for C_{Se} were analyzed using a flourometric technique. Some sample sites were located at or near flow gauging stations, operated by the Colorado Division of Water Resources (CDWR) or the United States Geological Survey (USGS). Data from these stations were used to estimate flow rates and storage changes within the river reaches. Measured EC values at river locations ranged from 0.58 to 4.30 dS/m upstream among 58 sample periods and from 1.44 to 4.73 dS/m downstream among 61 sample periods. Measured C_{Se} in the river downstream ranged from 5.4 to 21.1 μg/L among 12 sample periods. Daily average flow rates at river gauging stations ranged from near 0 (during extreme drought of 2002) to 49.0 m^3/s upstream and from near 0 to 17.3 m^3/s downstream.

Of the 11 sampled locations upstream, two were used to calculate in-stream loads at the reach endpoints in the development of the TDS mass balance model. The sampled location marking the upstream end of the reach was at the CDWR gauging station on the river below the Catlin Dam near Manzanola, Colo. (River 1). The location marking the downstream end was at the USGS station on the river at Las Animas, Colo. (River 4). Between these endpoints, four gauged canals (Canal 1–4) that divert water from the river and two gauged tributaries (Tributary 1, 2) were incorporated into the mass balance model. A third tributary flow consisted predominately of a permitted point discharge at the mouth of King Arroyo (Tributary 3). This point discharge was made up of the combined treated wastewater discharge and reverse osmosis effluent from the city of La Junta. Discharge data were obtained from the city of La Junta and measurements of EC were made in the field. A number of additional tributaries along both the upstream and downstream reaches were not gauged due to low or intermittent flows and/or due to financial limitations.

Two of the nine sampled locations in the downstream reach were used to calculate in-stream loads at the reach endpoints for the mass balance models of TDS and Se. The upstream location on the reach was at the USGS gauging station at Lamar, Colo. (River 5). The USGS gauging station on the river near Coolidge, Kan. (River 8) formed the downstream sampled location. Between these endpoints of the reach, there were three measured canals (Canal 5–7) diverting water from the river and two gauged tributaries (Tributary 4, 5).

The remaining sampled locations, two sites upstream (River 2, 3) and two downstream (River 6, 7), were near additional existing river gauging locations. Data at these sites were used in estimating changes in stored mass within each reach for each sample period, as discussed in the following section.

Methodology

Stochastic Mass Balance Models

In developing the mass balance, the control volume was the river reach with boundaries located around the river perimeter and at the upstream and downstream cross sections of each reach. The unknown variable calculated to bring closure to the mass balance along each river reach for each sample period was interpreted as an estimate of unmeasured NPS load associated with accumulated surface and groundwater flow to or from both ungauged tributaries and the main stem of the river. The total NPS load was then calculated by adding the measured NPS tributary inflow loads to the calculated unmeasured load. The unmeasured NPS load of a given constituent (either TDS or Se), L_{UNPS}, to a given river reach over a sample period, Δt (days), is

$$L_{\mathrm{UNPS}} = L_{R_{\mathrm{DS}}} + \sum_{j=1}^{N_0} L_{O_j} - L_{R_{\mathrm{US}}} - \sum_{k=1}^{N_I} L_{I_k} - \sum_{m=1}^{N_{\mathrm{PS}}} L_{\mathrm{PS}_m} + \frac{\Delta S}{\Delta t} + X \qquad (1)$$

wherein $L_{R_{\mathrm{DS}}}$=average outflow load over Δt through the downstream cross section on the river reach (kg/day); L_{O_j}=average load over Δt for jth measured canal diversion outflow from the river reach (kg/day); N_O=total number of measured outflow locations; $L_{R_{\mathrm{US}}}$=average inflow load over Δt through the upstream cross section (kg/day); L_{I_k}=average load over Δt for the kth measured NPS tributary inflow (kg/day); N_I=total number of measured inflow locations; L_{PS_m}=average load over Δt for the mth measured inflow from a permitted point-source discharge to the river reach (kg/day); N_{PS}=total number of permitted point-source discharges; ΔS=average change in stored constituent mass (kg) within the portion of the river reach Δt; and X=average net internal sink (+) or source (−) of constituent mass within the reach (kg/day) derived from dissolution and precipitation, adsorption/desorption to sediments, volatilization etc.

In the current analysis the random variable "X" was considered negligible, with the constituents of concern being mostly conservative in nature. The uncertainty in the values of each of the other input variables was assumed to be derived primarily from three types of ambiguity. The first type is associated with error in measuring various parameters associated with each variable at selected locations in space and time. The second is in using the values of these measured parameters to estimate values of other important parameters, employing supplemental data to describe relationships between the parameters. Usually, the selection of certain parameters for routine measurement, as opposed to estimation from derived relationships, is based upon the relative expense and utility of making in situ observations and/or sampling with followup analysis. The third type is due to the fact that measurements or estimations can be made for only a limited number of space-time points in a system subject to sizeable spatial and temporal variability. Hence, Eq. (1) constitutes a stochastic mass balance model, wherein each variable is random on a range of possible values that are governed by a probability distribution that depends in turn upon the probability distributions of the parameters. In general, these random variables may be correlated.

Several parameters associated with flow and solute concentration had to be estimated in order to quantify each of the input load variables in Eq. (1). These parameters were modeled as random, governed by probability distributions with statistical characteristics inferred from actual field data, by reference to the literature, or by communication with informed sources. The @RISK (version 4.5) software program was used to fit the probability distributions (using highest ranking distributions for combined chi-square, Kolmogorov–Smirnov, and Anderson–Darling goodness-of-fit tests) and to generate random values (RVs) out of the fitted or assumed distributions (Palisade Corporation 2005). The number of data points used in fitting distributions ranged from about 9 to 157 and averaged about 61 for the various parameters considered. Using Monte Carlo simulation in @RISK, a RV (i.e., realization) of each parameter was obtained by generating a value from its respective probability distribution using pseudorandom numbers. Each generated set of RVs for the parameters was used to calculate a corresponding RV for the set of input loads in Eq. (1). Finally, Eq. (1) was solved for a RV of the output random variable L_{UNPS}. An estimate of the total NPS load of a given constituent over a sample period, L_{NPS}, was then obtained as the sum of the calculated random unmeasured load and the random measured NPS tributary loads: $L_{\mathrm{NPS}}=L_{\mathrm{UNPS}}+\Sigma_{k=1}^{N_I} L_{I_k}$. Probability distributions were fit to the results of a total of 1,000 RVs, and statistics were computed, to signify the uncertainty in the respective output variables for each sample period for each river reach. This number of realizations was sufficient to attain convergence in the mean and standard deviation of the probability distributions of the output variables within about 5% for most cases (more than about 94%) and in the quantiles within about 10% for most cases.

Characterization of Uncertainty in Stream Loads

Different classifications of uncertainty have been suggested by researchers in different fields of study. The approach used in this study is based upon the taxonomy presented in Tung and Yen (2005) that describes the two most fundamental sources of uncertainty as "knowledge deficiency" and "natural variability." The random input variables, consisting of the inflow and outflow terms in Eq. (1), were modeled by accounting for parameter uncertainties derived from measurement error (a form of knowledge deficiency), spatial variability, and temporal variability (forms of natural variability), and ambiguity in the use of fitted regression equations (another form of knowledge deficiency). These several sources of uncertainty were systematically accounted for in arriving at possible values of the respective unknown random parameters and the calculation of the random loads in Eq. (1).

Measurement Error

A single instantaneous in situ EC measurement, designated as EC_1, was collected using a specific conductance probe during each sample period at each sampling location. The recorded value, EC_1, was assumed to be affected by instrument detection error and by error associated with the use of the probe to measure EC in flowing water at a location over a brief sampling interval of time.

Instrument detection error can be interpreted as the error present in detecting the EC of a small parcel of water with zero velocity relative to the probe. Due to the inherent limitations of the technology, the reading for EC displayed by the meter is not perfectly accurate. Instrument detection error was assumed characterized by a normal distribution with fifth and 95th quantiles at -0.5 and $+0.5\%$, respectively, from the displayed value, EC_1 (YSI 2001). A RV generated from this distribution, designated as EC_2, accounts for uncertainty due to detection error.

To further evaluate error in using specific conductance probes in the field, experiments were conducted using several probes to collect EC measurements at the same location and brief sampling interval (on the order of 5 s). The range of detected EC values was recorded as the probe was submerged in flowing water. The error in the use of the instrument to estimate an average over a brief sampling interval was quantified based upon the ranges of values displayed by the instrument and the average EC value over that range. It was found that the error could be described by assuming that the true value at the sample point within a cross section was normally distributed about a mean represented by the value EC_2, with a CV (absolute value of the ratio of the standard deviation to the mean) of 0.10. Accounting for this further measurement error in flowing water results in a RV designated as EC_3.

Water-quality samples for C_{Se} were collected as single instantaneous grab samples at the same locations as the EC samples along the downstream reach. Samples for C_{Se} were not gathered along the upstream reach. The concentration value reported by the laboratory for a grab sample, C_{Se_1}, was subject to error associated with the limitations of the fluorometric technique. This error was assumed to be normally distributed about a mean represented by C_{Se_1} with a CV of 0.05 (Nancy Thiex, Olson Biochemistry Labs, South Dakota State University; personal communication, October 26, 2006). A RV, C_{Se_2}, generated from this distribution, acknowledges the uncertainty derived from error in laboratory analysis.

It was further assumed that there is error in collecting a grab sample at a point within a cross section of a flowing waterway to represent the average concentration at that location over a brief interval of time. Similar to the treatment of uncertainty in measuring EC, it was assumed that the true value at the sample point was normally distributed about a mean represented by C_{Se_2}, with a CV of 0.10. Accounting for this further measurement error in flowing water results in a RV designated as C_{Se_3}.

Daily average flow rates, Q, in the river and in tributaries over a sample period were approximated using stage-discharge relationships developed by the USGS and the CDWR in conjunction with stage measurements taken at 1/2-h intervals. Average flow diversions to canals were similarly estimated using a flume with an appropriate rating equation and flow depth measurement taken on 15-min intervals. A Cipolleti weir equipped with an ultrasonic recorder and an electromagnetic meter were used to measure regulated point discharge of treated wastewater discharge and reverse osmosis effluent, respectively, into King Arroyo. The value of discharge calculated using a stage-discharge relationship, flume rating equation, weir rating equation, or electromagnetic meter calibration equation was designated as Q_1. It was assumed that the true instantaneous flow rate at a monitored stream location was a random parameter distributed normally about a mean represented by Q_1 with a CV of 0.05 (Rantz et al. 1982). Similarly, the flow rate for each canal was assumed to be a random parameter distributed normally about a mean signified by Q_1 calculated from the flume rating equation with a CV of 0.05. For permitted point discharge into King Arroyo, a CV of 0.03 was used for a normal distribution about the daily wastewater Q_1 measured with a Cipolleti weir and a CV of 0.01 was used about the daily reverse osmosis effluent Q_1 measured with an electromagnetic meter. The respective RVs of discharge generated by accounting for these errors were designated as Q_2.

Spatial Variability

Another source of uncertainty was due to the use of a value measured near the midpoint of a cross section in a stream to represent the average value over the entire cross section. Based upon field observations, average EC over the stream cross section at a sample location and time, EC_4, was modeled as a random parameter normally distributed about a mean value represented by EC_3, and having a CV of 0.05. The same probability distribution was assumed suitable to describe uncertainty due to spatial variability over the cross section in values of C_{Se}. A RV of average concentration, C_{Se_4}, was generated using the value of C_{Se_3} to signify the mean.

Temporal Variability

Each instantaneous EC measurement at a sample location was used to estimate the average EC value at that location over the entire sample period, a common practice in studies of this type. A statistical analysis was performed to quantify the level of uncertainty in using data available from a single USGS gauging station within each river reach, where EC was measured at a point within the cross section on 1/2-h increments. These "continuous" USGS EC measurements were averaged over each sample period and compared with the instantaneous field EC measurements taken at or near the same locations within each sample period. A residual was then calculated as the difference between the average of the "continuous" EC measurements and the instantaneous EC value measured in this study. A positive or negative residual value indicated whether the measured value underestimated or overestimated the average EC value, respectively. To account for a possible relation between the size of the residual and the size of the measured EC value, the ratio, ε_{EC}, of the residual value to the instantaneous measured value was calculated for each sample period at each gauging location. Separate probability distributions for the gauging station sites in the upstream and downstream reaches were fit for these ratios in order to characterize the error in using an instantaneous measure of EC to represent the temporal average EC over a sample period at all sites within the upstream and downstream reaches, respectively. The probability distributions were inferred from multiple values of ε_{EC} across the sample periods at a given gauging location. This analysis was conducted separately for sample periods of 1-, 2-, and 3-day durations at each gauging site. For the upstream reach, the residual ratios were found to have best-fit logistic probability distributions with mean=0.003 and CV=32.58, mean=−0.016 and CV=11.97, and mean=0.082 and CV=3.36 for 1-, 2-, and 3-day sample periods, respectively. The computed residual ratios for the 1- and 2-day sample periods at the gauging site downstream were found to be statistically similar. Hence, the data were pooled and fit to a gamma distribution with mean=−0.024 CV=4.38, and skewness coefficient (SC)=0.41 for use for both the 1- and 2-day sample periods (no 3-day sample periods were analyzed downstream). Hence, a RV of the average EC over a sample period, EC_5, was calculated as the following random function of the instantaneous average EC over the cross section, EC_4

$$EC_5 = EC_4(1 + \varepsilon_{EC}) \tag{2}$$

A similar relationship was also developed to describe the temporal variability of C_{Se} values.

Correlation between Q_1 and ε_{EC} also was calculated at each of the "continuous" gauge sites and for sample periods of differing duration to explore the possibility that higher Q_1 values would correspond to higher or lower ε_{EC} values. The Pearson correlation coefficient was found to have a weak, but statistically significant, value of −0.36 for 2-day periods upstream and was statistically insignificant downstream. Hence, correlation with Q_1 was incorporated in generating RVs of ε_{EC} for use in Eq. (2) only for 2-day sample periods upstream.

Ambiguity in Regression Relationships

Surface water samples were gathered in the field and were analyzed to estimate the relationship between TDS (mg/L) concentration and EC (dS/m). For the upstream reach, the following empirical regression model was estimated

$$TDS = 685.9EC_5 + 128.0 \quad (r^2 = 0.97) \tag{3a}$$

To account for error in the fitted regression model, Eq. (3*a*) was amended to obtain

$$TDS = (685.9EC_5 + 128.0)(1 + \varepsilon_{TDS}) \tag{3b}$$

wherein ε_{TDS}=random parameter of the ratio of the residual error to the predicted TDS. Values of residual error were estimated as the difference between values of TDS determined in the laboratory and values predicted by Eq. (3*a*) using corresponding observed values of EC_1, rather than values for EC_5. The residual ratio, ε_{TDS}, for the upstream data set was found to have a log-logistic probability distribution (mean=−0.037, CV=4.97, SC=0.81). In a similar fashion, a regression relationship (r^2=0.95) was developed using a data set for downstream and was applied within the following model

$$TDS = 728.7EC_5^{1.10}(1 + \varepsilon_{TDS}) \tag{4}$$

wherein ε_{TDS} was found to have a log-logistic probability distribution (mean=0.002, CV=36.41, SC=0.33) for the downstream data set. Finally, RVs of daily loading rates of TDS were calculated by multiplying the average TDS values [predicted by Eqs. (3*b*) and (4)] by corresponding random average daily flow rates over the sample period at each respective location.

For analyzing the Se mass balance along the downstream river reach, a regression relationship (r^2=0.77) was fit using a sample set of measured EC and C_{Se}(μg/L) estimated in the laboratory from grab samples taken at three stations along the river located near USGS gauging stations at which "continuous" (1/2-*h* interval) EC measurements were made. This relationship was applied within the following model

$$C_{Se_5} = 2.3EC_1^{1.23}(1 + \varepsilon_{C_{Se}}) \tag{5}$$

wherein $\varepsilon_{C_{Se}}$=random residual ratio with a logistic probability distribution (mean=0.017, CV=10.36). Eq. (5) was used to convert the USGS "continuous" EC_1 measurements to corresponding estimates of "continuous" C_{Se_5} values. These "continuous" C_{Se_5} estimates were then averaged over each sample period and compared with the instantaneous C_{Se_4} values obtained from analysis of grab samples at the same locations within each sample period. A relationship similar to Eq. (2) for modeling uncertainty due to temporal variability was then developed for use in calculating a RV of the average over a sample period, C_{Se_6}, as a random function of the instantaneous value averaged over the cross section, C_{Se_4}. The random residual ratios, $\varepsilon'_{C_{Se}}$, in this relationship were found to have a logistic distribution (mean=−0.172, CV=0.69). Finally, RVs of loading rates of Se were calculated by multiplying a realization of estimated average C_{Se_6} values over the period by a realization of the average daily flow rate over the sample period at each respective location.

The probability distributions assigned to each of the random parameters used in this study were truncated at the first and 99th quantile values. This was to exclude physically unrealistic extreme values.

Steps in Computing Random Values of Stream Loads

The following list summarizes the successive steps, described in the preceding, that were used in computing a RV of TDS load at a stream location over a sampling period:

1. Obtain instantaneous field measurement, EC_1, near middle of cross section;
2. Generate RV of instrument detection error and add to EC_1 to obtain RV of EC_2;
3. Generate RV of sampling error in flowing water and add to EC_2 to obtain RV of EC_3;
4. Generate RV associated with spatial variability over cross section and add to EC_3 to obtain RV of EC_4;
5. Generate RV associated with temporal variability over sample period and add to EC_4 to obtain RV of EC_5;
6. Enter EC_5 in stochastic EC-TDS regression equation to obtain RV of TDS;
7. Compute flow rate Q_1 from appropriate stage-discharge rating equation for the site;
8. Generate RV of rating equation error and add to Q_1 to obtain RV of Q_2; and
9. Compute RV of TDS load=(TDS)(Q_2).

The successive steps used in computing a RV of Se load at a stream location over a sampling period are summarized as follows:

1. Obtain instantaneous field measurement (grab sample) near middle of cross section and analyze in laboratory to obtain C_{Se_1};
2. Generate RV of laboratory analysis error and add to C_{Se_1} to obtain RV of C_{Se_2};
3. Generate RV of sampling error in flowing water and add to C_{Se_2} to obtain RV of C_{Se_3};
4. Generate RV associated with spatial variability over cross section and add to C_{Se_3} to obtain RV of C_{Se_4};
5. Account for uncertainty due to temporal variability over the sample period:
   a. Estimate averages over sample period, C_{Se_5}, using stochastic EC-C_{Se} regression equation and compare with estimates obtained from instantaneous grab samples to calculate residual errors associated with temporal variability and
   b. Generate RV of error associated with temporal variability and add to C_{Se_4} to obtain a RV of C_{Se_6};
6. Compute flow rate Q_1 from appropriate stage-discharge rating equation for the site;
7. Generate RV of rating equation error and add to Q_1 to obtain RV of Q_2; and
8. Compute RV of Se load=(C_{Se_6})(Q_2).

Characterization of Uncertainty in Mass Storage Change

No previous studies are known to have accounted for storage change in estimating NPS loads, but instead have assumed essentially steady-state conditions along the river. In general, stored mass is accumulated or depleted along a river reach associated with changes in flow depth due to unsteady flow and with changes that occur in the hydraulic geometry of the stream. Uncertainty associated with $\Delta S/\Delta t$ for the entire reach was estimated by accounting for several random parameters. In evaluating the $\Delta S/\Delta t$ term, each reach was divided into three segments with USGS or CDWR gauging stations marking the boundaries. The volume of water within each of the segments was calculated using incremental measurements of flow depth, h_1, ranging from 15-min to 1-h sampling intervals throughout each sample period. Per communication with the USGS and CDWR, the random parameter of the true flow depth, h_2, was estimated as normally distributed with fifth and 95th quantiles at 0.003 m (0.01 ft) below and above a mean represented by h_1, respectively.

Survey data of channel cross-section geometry were obtained from USGS and CDWR for measurements made over the period 1999–2005 at each of the four stations included in the storage change analysis for each reach. These data were used to develop regression relationships between top width at the water surface, T_w, and h_2. Following Gates and Al-Zahrani (1996a,b) and Buhman et al. (2002), a power function was developed, using non linear regression, for each gauging station based upon the cross-sectional geometry of the river at that station, with r^2 values ranging between 0.43 and 0.84. The regression relationship developed at each station was incorporated into a model of T_w as a random function of h_2

$$T_w = t_1 h_2^{t_2}(1 + \varepsilon_{T_w}) \tag{6}$$

In Eq. (6), t_1 and t_2 were modeled as random parameters due to spatial and temporal variability in the size and shape of the cross-section geometry along the river. Insufficient cross-section surveys were available to infer the statistical characteristics of these parameters, so reference was made to previous studies. Based upon similar power relationships developed by Gates and Al-Zahrani (1996b) for river reaches of comparable size to those in this study, the parameters were assumed normally distributed with CV values of 0.7 for t_1 and 0.5 for t_2. The mean values at each station were assumed to be represented by the values derived from regression analysis at that station. Mean values for t_1 ranged from 3.81 to 96.37 upstream and from 3.60 to 22.19 downstream. Mean values for t_2 ranged from 0.93 to 3.10 upstream and from 0.25 to 2.56 downstream. Based upon a study by Buhman et al. (2002), t_1 and t_2 were assumed inversely correlated with a Pearson correlation coefficient of −0.60. The parameter ε_{T_w} in Eq. (6) is a residual ratio associated with the error in fitting the regression equation to data at a given station (Buhman et al. 2002). The probability distribution of ε_{T_w} was inferred from the survey data set at each cross section by comparing observed values of T_w to values computed using the power term, $t_1 h_1^{t_2}$. The best fit distributions were logistic (mean=−0.004, CV=69.83), beta general (mean=−0.045, CV=8.40), log logistic (mean=−0.044, CV=6.91), and Weibull (mean=−0.025, CV=11.91) for the four cross sections upstream and were triangular (mean=−0.065, CV=4.98), Weibull (mean=−0.0003, CV=363.34), triangular (mean=−0.018, CV=14.21), and Weibull (mean=−0.015, CV=10.48) downstream. Probability distributions were skewed with SC values ranging from −0.76 to 3.88. For each RV of h_2 realized in association with measurements at the beginning and end of each sample period, a RV of T_w was estimated using Eq. (6). A corresponding random change in cross-sectional area of flow at each gauging station was calculated as the product of the average T_w estimated at the beginning and end of the sample period and the change in h_2 over the period. Computed RVs accounted for measurement and estimation error and for spatial and temporal variability in the cross-sectional geometry along the analyzed river segments.

The average change in cross-sectional flow area over a sample period over an entire river segment was estimated as the arithmetic average of the changes computed at the ends of the segment. The true segment-averaged change in flow area was assumed to be normally distributed with a CV of 0.20 about a mean represented by this change in flow area computed using only the two end points. The net change in flow volume over a sample period for each segment within each reach was estimated as the average of the computed flow area change multiplied by the length of the segment along the river thalweg axis. The true length of the segment was estimated to be a normally distributed parameter with a CV of 0.05 about a mean represented by a value obtained by digital tracing of the river length from satellite images.

Segment-averaged values of TDS and C_{Se} were estimated as normally distributed about a mean signified by the arithmetic average of the respective random realizations of the average values over the sample period at the ends of each segment, computed as described in the preceding section. The CV of this normal distribution was assumed to be 0.05 for TDS and 0.10 for C_{Se}. These segment-averaged concentrations were multiplied by the computed change in flow volume over each respective segment and divided by the number of days in the sample period to yield a RV of the time rate of change in stored solute mass within each segment for each sample period. These values within each segment were then added together to estimate a RV of $\Delta S/\Delta t$ for the entire river reach.

Analysis of Sensitivity to Parameter Uncertainty

To estimate the degree to which the uncertainty in each random parameter influences the uncertainty in the computed values of the total NPS loads, the CV values of the probability distributions of each random parameter were adjusted between two limits. A sensitivity scenario consisted of changing the CV values for a single random parameter to a value representing a factor of 0.5 and 2 times the originally-estimated, or baseline, CV values described in previous sections. The CV values of the calculated total NPS loads averaged over all available sample periods corresponding to both respective factors of the considered parameter CV value were designated as $\overline{\mathrm{CV}}_{0.5}$ and $\overline{\mathrm{CV}}_2$. A measure of uncertainty sensitivity in the computed total NPS load associated with each random parameter was evaluated as

$$S_{\mathrm{CV}} = \frac{|\overline{\mathrm{CV}}_2 - \overline{\mathrm{CV}}_{0.5}|}{\overline{\mathrm{CV}}_1} \tag{7}$$

wherein $\overline{\mathrm{CV}}_1$=baseline CV value of the computed NPS loads averaged over all sample periods. The value of S_{CV} indicates the relative influence that change in the degree of uncertainty of a given random parameter has on the degree of uncertainty in the computed load.

For the NPS TDS load calculations, sensitivity Scenario A considered changes in CV values for instrument detection of EC_2.

Table 1. Averages of Statistics of Calculated Unmeasured and Total NPS TDS Loads to Arkansas River along Upstream Reach Assuming Baseline CV Values in Probability Distributions of Random Parameters

	Annual average statistics					
NPS load	Mean [(kg/day)/km]	CV	5th Quantile [(kg/day)/km]	95th Quantile [(kg/day)/km]	90% prediction interval width [(kg/day)/km]	Common best-fit probability distributions
2000 unmeasured	10,924	0.56	2,785	19,765	16,980	Log normal
2000 total	13,690	0.41	5,584	22,500	16,916	Beta general/inverse Gaussian/ log logistic/Pearson IV
2001 unmeasured	7,244	0.62	503	14,101	13,598	Beta general/log normal
2001 total	10,281	0.40	3,672	17,053	13,382	Normal/beta general/log normal
2002 unmeasured	3,783	0.93	1,299	6,640	5,341	Beta general/logistic/Weibull
2002 total	4,515	1.78	2,059	7,349	5,290	Weibull/logistic/normal/Pearson IV
2004 unmeasured	3,822	2.62	−5,010	12,060	17,070	Inverse Gaussian/logistic/normal/Weibull
2004 total	6,063	1.47	−2,718	14,267	16,985	Inverse Gaussian/log logistic/normal/Weibull
2005 unmeasured	3,175	3.14	−7,209	13,257	20,465	Weibull
2005 total	5,164	2.29	−5,179	15,221	20,400	Weibull
Overall average: unmeasured	6,227	1.32	−597	13,193	13,790	Weibull
Overall average: total	8,383	1.13	1,617	15,308	13,691	Weibull

For the Se load calculations, Scenario A addressed changes in CV values of the point measurement, C_{Se_2}, associated with laboratory error. Scenario B considered changes in the CV values for the distribution of EC_3 around the recorded instrument reading in flowing water or for C_{Se_3} around the laboratory-determined value. Scenario C depicted changes in the CV values of the average EC_4 (or C_{Se_4}) over the cross section, and Scenario D considered changes in the CV of the residual ratio, ε_{EC} for the average EC_5 (or the residual ratio for C_{Se_6}) over the sample period. Scenario E considered changes in the CV of the residual ratio ε_{TDS} for estimating TDS (or $\varepsilon_{C_{Se}}$ for estimating C_{Se_5}) from EC. Scenario F addressed changes in the CV values of the distribution of flow rate, Q_2. Scenario G adjusted CV values of the distribution for the flow depth, h_2, used in calculating the storage change input variable. Scenarios H and I addressed changes in the CV values of the channel top width parameters t_1 and t_2, respectively. Changes in the CV of the residual ratio for estimating T_w from h_2, using Eq. (6), was addressed in Scenario J. In Scenario K, the CV values for the segment-averaged flow area were adjusted. For Scenario L, the range of CV values of the segment length distribution was altered. In Scenario M, the CV values characterizing the probability distribution of the segment-averaged TDS were adjusted.

Results and Discussion

Unmeasured and total NPS load values were calculated using a stochastic mass balance model for each available sample period, as discussed above. Results are presented for TDS loads upstream and downstream and for Se loads downstream.

Uncertainty Analysis of TDS Loads in Upstream Reach

Using baseline CV values in the probability distributions of the random parameters, probability distributions and associated statistics were estimated for the resulting 1,000 realizations of predicted unmeasured NPS TDS loads and total NPS TDS loads within each period. Table 1 presents the most common best-fit probability distributions and average values (over the sample periods within each year) for the following statistics for the upstream reach: mean, CV, fifth, and 95th quantile, and 90% prediction interval width. The 90% prediction interval width was calculated as the difference between the fifth and 95th quantile values of the predicted loads. It is estimated that there is a 90% probability that the true (but unknown) value of the unknown NPS load lies within the interval between the fifth and 95th quantile values, and the interval width serves as an indicator of the magnitude of the spread in the possible load values.

Net unmeasured and total inflow loads (or sources) are designated as positive, and outflow loads (or sinks) as negative. Negative values for the mean of the total NPS TDS loads, indicating outflow loads, only occurred during one sample period in 2002, two in 2004, and one in 2005, perhaps indicative of effects of the drought period. All of the other predicted mean values in the upstream reach were positive, indicating net inflows to the river. The highest annual average of the mean values for total NPS TDS inflow loads occurred in 2000 at 13,690 (kg/day)/km, whereas the smallest annual average of the mean values occurred in 2002 at 4,515 (kg/day)/km.

Total NPS loads along a river reach are expected to vary over time for several reasons. First, hydrologic conditions in the river valley vary considerably over time, resulting in variability in rainfall, in total water volumes diverted to canals for application to irrigated lands, in groundwater well pumping rates, and in evapotranspiration, leading to variability in surface and subsurface return flow rates. Second, concentrations in flows diverted from the river fluctuate considerably over time. Third, processes that determine rates of dissolution of salts and Se from subsurface marine shales and shale-derived soils vary with varying recharge from irrigation, with well pumping rates, and with varying properties associated with chemical weathering, solubility, mobilization, and transport. Last, and less influential, is variability in salts derived from application of fertilizers to irrigated lands. The magnitude of temporal variability associated with these issues is also dependent on the season of the year.

The mean value of NPS TDS load averaged over all 58 sample periods was 8,383 (kg/day)/km. The average annual CV values ranged from 0.40 to 2.29 for the total NPS TDS load predictions. The average 90% prediction interval width was substantial com-

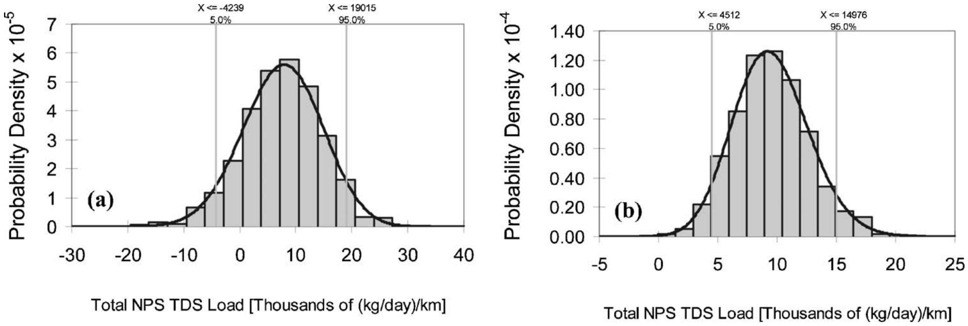

Fig. 3. Frequency histogram and best-fit distribution of total NPS TDS loads to Arkansas River along upstream reach for sample periods: (a) June 7–8, 2000 (beta general distribution); (b) August 2–3, 2004 (inverse Gaussian distribution)

pared to the average computed mean loads, taking its largest value of 20,400 (kg/day)/km in 2005, and its smallest value of 5,290 (kg/day)/km in 2002.

These results seem reasonable when compared to the total salt loads applied to the irrigated alluvial land flanking the upstream study reach. Using records of daily flow diversions to canals and average salt concentrations in the canals (Gates et al. 2006), a deterministic average salt load diverted to the land was estimated as about 7,200 (kg/day)/km over the period 2000–2004. Salt loads in return flows are likely markedly larger than those applied to the land due to the additional salts picked up by dissolution as subsurface flows make their way back to the river (Burkhalter and Gates 2005; Gates et al. 2006).

The ratio of the mass storage change within the river reach to the total NPS TDS load was calculated for each considered realization within each sample period. The annual averages of the mean of these calculated ratios ranged from 0.33 in 2001 to 2.47 in 2002, indicating that mass storage change within the river reach is a major factor in estimating NPS TDS loads and should not be neglected.

The best-fit probability distributions for the predicted total NPS TDS loads in the upstream reach were skewed for 79% of the considered sample periods. The SC values for these skewed distributions ranged from −0.79 to 1.27. Example frequency histograms and fitted probability distributions for the total NPS TDS load for June 7–8, 2000 and for August 2–3, 2004 are shown in Fig. 3, illustrating the typical skew in the computed values. The box plot in Fig. 4 illustrates statistical characteristics, including spread of the 90% prediction interval, for the computed total NPS TDS loads for all of the available sample periods for the upstream study reach.

Uncertainty Analysis of TDS Loads in Downstream Reach

As in the upstream reach, statistics of the computed realizations of unmeasured NPS TDS loads and total NPS TDS loads for baseline CV values in the probability distributions of the random parameters were computed and averaged over the sample periods within each year downstream. Negative values for the mean of the total NPS TDS loads were computed for three sample periods in 2002; values for all other periods were positive. The annual average of the mean values for inflow loads ranged between 8,121 (kg/day)/km in 2003 and 14,578 (kg/day)/km in 2004. The overall average mean across the 61 sample periods was 11,183 (kg/day)/km. The average annual CV values ranged from 0.15 to 2.76 for the total NPS TDS load predictions. Similar to the upstream reach, the average 90% prediction interval width for the downstream reach was rather large, ranging from 4,919 (kg/day)/km in 2003 to 11,806 (kg/day)/km in 2006. For comparison, records of daily flow diversions to canals and average salt concentrations periodically measured in the canals (Gates et al. 2006) were used to obtain a deterministic estimate of 14,800 (kg/day)/km for the average salt load diverted to the valley land flanking the downstream study reach over the period 2002–2004.

Sampling periods along the upstream and downstream reaches were closely contemporaneous from April to September 2002, from May to August 2004, and from June to July 2005. The computed mean value of total NPS TDS loads averaged over all of these periods was 11,591 (kg/day)/km for the downstream reach, or about 130% greater than the average mean of 5,066 (kg/day)/km for the upstream reach. A primary reason for this difference, in addition to variations in return flow rates associated with natural and man-induced hydrologic processes, is the markedly higher salt concentration in ground and surface waters of the downstream reach compared to upstream. Data from alluvial groundwater monitoring wells over these same periods (Gates et al. 2006) reveal average concentrations about 70% higher downstream compared to upstream. Average measured salt concentrations in the river were about 165% greater along the downstream reach compared to the upstream for these periods. These concentration differences between the two reaches are due

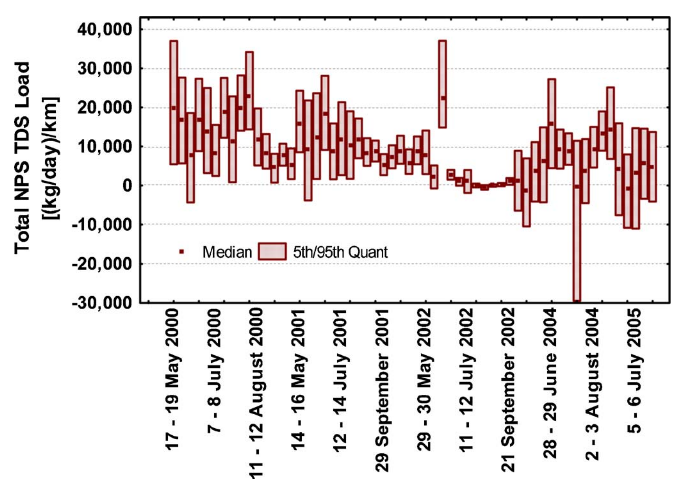

Fig. 4. Box plot of distribution of total NPS TDS loads to Arkansas River along upstream reach for all sample periods from 2000 to 2005

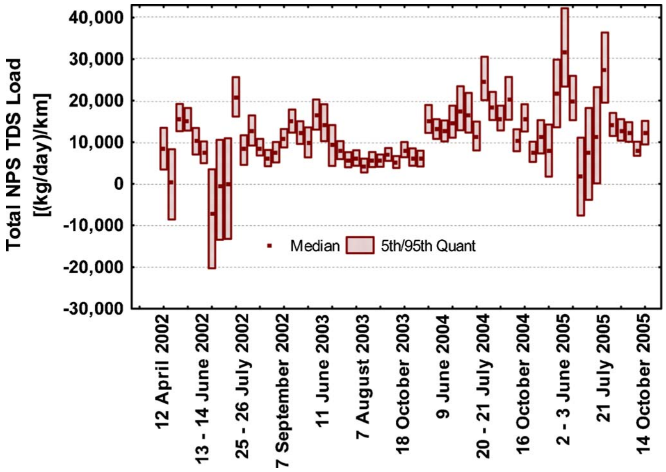

Fig. 5. Box plot of distribution of total NPS TDS loads to Arkansas River along downstream reach for all sample periods from 2002 to 2005

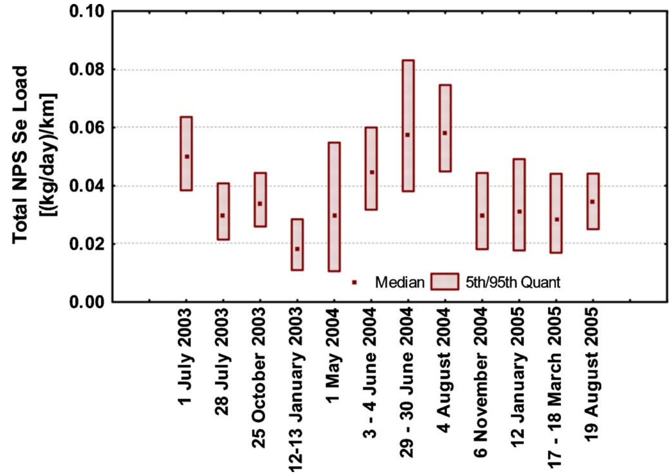

Fig. 6. Box plot of distribution of total NPS Se loads to Arkansas River along downstream reach for all sample periods from 2002 to 2005

primarily to increasing evapoconcentration along the downstream direction, to differing salt dissolution rates associated with variable subsurface marine shales and shale-derived soils along the valley, and to precipitation of gypsum salts in areas where the solubility constant has been exceeded.

The annual averages of the mean of the ratio of the mass storage change to the total NPS TDS load ranged from 0.05 in 2004 to 0.48 in 2005 for the downstream reach. As in the upstream reach, mass storage change can constitute a substantial component of mass balance calculations.

The best-fit probability distributions for the predicted total NPS TDS loads were skewed for 89% of the sample periods considered. The SC values for these skewed distributions ranged from −0.38 to 0.94. The box plot in Fig. 5 illustrates statistical characteristics and spread for the computed total NPS TDS loads for all of the available sample periods for the downstream reach.

Uncertainty Analysis of Se Load in Downstream Reach

Table 2 summarizes the best-fit probability distributions and associated statistics of the predicted stochastic total NPS Se loads using baseline CV values in the probability distributions of the random parameters. The magnitudes of the Se loads are far smaller than the TDS loads, due to the correspondingly smaller concentrations. The overall average mean load over all sample periods was 0.038 (kg/day)/km, and the overall average CV was 0.23. The overall average 90% prediction interval width was 0.028 (kg/day)/km, reflecting considerable variability in predicted values of Se load. Skewed probability distributions, with SC values ranging from 0.08 to 0.65, were fit to the 1,000 predicted values for total NPS Se load for all of the sample periods. A box plot of the distribution of predicted values for each of the available sample periods is provided in Fig. 6.

Butler and Leib (2002) reported in-stream Se loads at 52 locations in the tributaries and main stem of the lower Gunnison

Table 2. Statistics of Calculated Total NPS Loads of Se to Arkansas River along Downstream Reach Assuming Baseline CV Values in Probability Distributions of the Random Parameters

	Statistics of total NPS Se load					
Sample period	Mean [(kg/day)/km]	CV	Fifth quantile [(kg/day)/km]	95th quantile [(kg/day)/km]	90% prediction interval width [(kg/day)/km]	Best-fit probability distribution
July 1, 2003	0.051	0.15	0.039	0.064	0.026	Beta general
July 28, 2003	0.030	0.20	0.021	0.041	0.019	Gamma
October 25, 2003	0.035	0.16	0.026	0.044	0.018	Inverse Gaussian
January 12–13, 2003	0.019	0.28	0.011	0.029	0.017	Inverse Gaussian
May 1, 2004	0.031	0.44	0.010	0.054	0.044	Log normal
June 3–4, 2004	0.045	0.19	0.032	0.060	0.028	Pearson
June 29–30, 2004	0.059	0.24	0.038	0.084	0.046	Gamma
August 4, 2004	0.059	0.16	0.045	0.075	0.030	Inverse Gaussian
November 6, 2004	0.030	0.26	0.018	0.044	0.026	Log normal
January 12, 2005	0.032	0.30	0.018	0.049	0.031	Gamma
March 17–18, 2005	0.029	0.27	0.017	0.044	0.026	Pearson
August 19, 2005	0.034	0.16	0.025	0.044	0.018	Log normal
Overall average	0.038	0.24	0.025	0.053	0.028	Gamma/inverse Gaussian/log normal

Table 3. Computed Measure of Uncertainty Sensitivity, S_{CV}, for Considered Sensitivity Scenarios for Total NPS TDS Load along Upstream (US) Reach of Arkansas River and for Total NPS TDS and Se Loads along Downstream (DS) Reach (Top Three Values Highlighted in Bold for Each Case)

Sensitivity scenario	S_{CV} for US TDS	S_{CV} for DS TDS	S_{CV} for DS Se
A	0.03	0.01	0.08
B	0.15	0.38	**0.27**
C	0.04	**1.00**	0.08
D	**0.45**	**1.90**	**0.50**
E	**0.61**	0.30	**0.67**
F	0.04	0.26	0.08
G	0.00	0.00	0.00
H	0.14	**1.20**	0.00
I	**2.33**	0.45	0.01
J	0.05	0.09	0.00
K	0.02	0.15	0.00
L	0.01	0.02	0.03
M	0.00	0.00	0.00

River in Colorado, using flow and concentration data gathered intermittently over the period 1988–2000. Using their reported mean in-stream load of 22.0 kg/day in the Gunnison River above Escalante Creek and 25.1 kg/day in the Gunnison River at Whitewater (the upstream and downstream ends, respectively, of a 50-km reach of the river) and assuming negligible storage change yields an estimated total NPS load of about 0.062 (kg/day)/km. The NPS load along the Gunnison River would be expected to be larger than that along the Arkansas River, due to the extensive and more highly seleniferous Upper Cretaceous Mancos Shale present in the Gunnison valley, compared to the Upper Cretaceous Pierre Shale and Niobrara formations present in the Arkansas River watershed.

Sensitivity Analysis of Uncertainty in TDS and Se Loads

Estimated values of S_{CV} are summarized in Table 3 for each of the sensitivity scenarios considered for total NPS TDS load along the two study reaches and for total NPS Se load along the downstream reach. Consideration of the relative values of S_{CV} among scenarios reveals that the CV in calculated total NPS TDS loads was most sensitive to the CV in the residual ratio associated with estimating sample period average concentrations using instantaneous measurements and in the channel top width parameters used to calculate mass storage change along the river reach. For calculated Se loads, the CV was most sensitive to CV in the residual ratio associated with estimating sample period average concentrations using instantaneous measurements and in the residual ratio associated with the regression relationship for estimating C_{Se} from EC measurements.

Summary and Conclusions

Quantification of NPS loads to rivers, for the purpose of understanding and managing their effects on river concentrations, is critically important to environmental enhancement yet it remains elusive, largely due to high levels of uncertainty. Assessing uncertainty is important in using estimates to set regulatory standards on loading limits to rivers, such as TMDLs. It is also important in making decisions about engineering interventions, such as structural changes and BMPs, needed to manage loads to comply with regulations and with other performance criteria. The degree of confidence or reliability attached to the call for such regulation or intervention is indirectly related to the magnitude of CVs and of specified prediction interval widths.

In this representative field study, NPS loads to reaches along the Arkansas River were modeled as stochastic variables in a mass balance that depended upon uncertainty in model parameters derived from measurement error, spatial variability, temporal variability, and ambiguity in relationships between parameters. Analyses of the loads were based in part upon the examination of actual data collected from an extensive field effort and upon information derived from related studies. Expected values and uncertainties in NPS loads of TDS and Se, associated with natural and irrigation-induced flow and transport processes, were both found to be substantial. Moderate to high CVs and 90% prediction interval widths highlight the need for careful consideration of risk when contemplating interventions based upon NPS estimates derived from mass balance analysis of field measurements.

A very influential variable contributing to the calculated quantity of total NPS loads was the change in TDS or Se stored within the river reach over the sample period. Neglecting to account for such changes in storage when developing a mass balance model could lead to grossly inaccurate calculations.

Sensitivity analysis provided insight in assessing which input parameter uncertainties were most influential in determining the uncertainty of calculated NPS loads. Parameter uncertainties that were most prominent were those associated with estimating sample period average concentrations using instantaneous measurements, those related to channel geometry measurements for calculation of mass storage change along the river reach, and those associated with a regression relationship for estimating concentration from EC measurements. It may be worthwhile to invest more resources and manpower in clarifying and/or reducing the level of uncertainty in these parameters.

These findings will provide important data for the use of regional and basin-scale computational models designed to help decision makers select alternative measures for reducing NPS loads and thereby meet targets for reduced TDS and Se concentrations in the Arkansas River. Strategies currently under consideration include improving irrigation efficiencies to reduce recharge from overirrigation, lining canals to cut down on seepage, and altering pumping patterns (Burkhalter and Gates 2006). Possible effects of altered river operations, including changes in reservoir storage releases, and water leasing and exchange arrangements, on NPS loads and river concentrations, also are being examined.

Future investigations of NPS load uncertainty should consider possible internal sinks and sources that were neglected in the current mass balance model. An importance assessment should be conducted of the need for enhanced and more frequent sampling, especially of parameters to which NPS load estimates appear most sensitive. Refinements are also needed in the inference of the statistical characteristics of random parameters, including correlation structure. The effect of misspecification of the mass balance model itself, due to the neglect or inadequate description of flow, transport, and chemical reaction processes, should also be examined.

Acknowledgments

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